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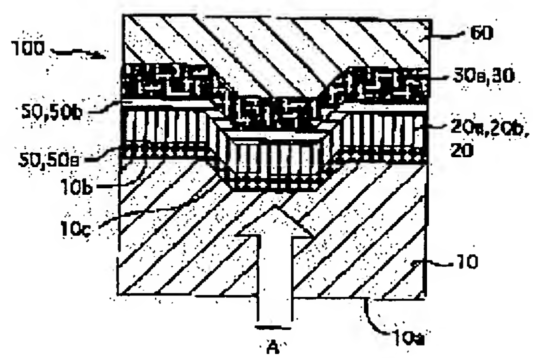
(54) LIGHT RECORDING MEDIUM

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a light recording medium, prominent in durability and recording characteristics.

SOLUTION: The light recording medium 100 is constituted of a recording layer having a first layer 20 containing Sn and Bi; a second layer 30 approximated to the first layer 20 and reacted with the first layer 20 by providing the same with an external energy; and an oxidizable layer 50 containing an oxidizable substance, readily oxidized compared with Sn and Bi and laminated on the first layer 20. An Sn-Bi alloy is prominent in recording characteristics and the second layer 30, reacted with the Sn-Bi alloy, and laminated whereby chemical characteristics are readily changed by the reaction between the first layer 20 and the second layer 30, thereby improving the recording characteristics. On the other hand, the oxidizable layer 50 containing the oxidizable substance, more readily oxidized than Sn and Bi, is laminated on the first layer 20 whereby the oxidizable layer 50 is oxidized selectively, thereby delaying the corrosion of the Sn-Bi alloy and improving the durability of the same.



* NOTICES *

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2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the optical recording medium which changes the optical property of a recording layer and records information by giving external energy. It is related with the optical recording medium which can be especially used for a recordable compact disk (CD-R), DVD-R, etc. in detail.
[0002]
[Description of the Prior Art]By giving external energy, the optical recording medium used for CD-R etc. changes the optical property of a recording layer, and records information. Therefore, excelling in optical properties, such as reflectance of a recording layer, changing easily at the time of record, i.e., a recording characteristic, and excelling [both] in the ability of the optical property of a recording layer not to change easily at the time of non recording, i.e., endurance, are called for.
[0003]That is, in an optical recording medium, at the time of the record to which external energy is given, a reaction needs to arise physically and/or chemically in a recording layer, and it is necessary to change optical properties, such as the reflectance. And it is necessary to maintain the optical property as it is, without a reaction arising in a recording layer in the time of non recording. Therefore, from a viewpoint of a recording characteristic and endurance, at the time of record, and the reaction arose on the /chemicals target, the optical property changed to him, and a reaction did not carry out raw at the time of non recording, but development has been furthered about the material and composition of a recording layer from which an optical property does not change.
[0004]For example, the optical recording medium using thin films laminated by the layer of Sn-Bi alloy and the layer of this Sn-Bi alloy, such as germanium, Cr, Ti, and nickel, is proposed by JP,6-78033,B. A recording characteristic and oxidation resistance improve by using the layer

of Sn-Bi alloy for a recording layer, and it is the technique of raising oxidation resistance further by laminating the layer (thin film) of the metal or semimetal which becomes a layer of Sn-Bi alloy from germanium etc. Namely, the invention indicated to JP,6-78033,B, While making easy change of the optical property at the time of record by using the layer of Sn-Bi alloy for a recording layer, change of the optical property by the oxidation at the time of non recording, etc. is controlled, Change of the optical property by the oxidation at the time of non recording, etc. is further controlled by laminating thin films, such as germanium, in the layer of Sn-Bi alloy.

[0005]

[Problem(s) to be Solved by the Invention]However, in the invention indicated to JP,6-78033,B, Though the optical change by the oxidation at the time of non recording, etc. can be controlled to some extent, by giving external energy, the layer of Sn-Bi alloy is bearing changing an optical property and recording information, its non-Records Department reflectance is low, and it cannot necessarily be said to be enough about a recording characteristic. It is hard to say that it has not necessarily high endurance.

[0006]Using Sn-Bi alloy as a recording layer as a result of research recognized this invention person to be effective as follows in respect of improvement in a recording characteristic.

[0007]that is, when forming Sn-Bi alloy on a substrate, although Sn-Bi alloy is recrystallized on a substrate face, since it is metal of eutectic crystal nature, the grain growth of the particle is boiled to some extent, until control is carried out, and a layer is formed rather than growth of particles by the increase in a particle number. It becomes that in which the shape of the recording layer was ready as a result. The noise level of an optical medium falls by this, the characteristic degradation of C/N (ratio of the output level of carrier to noise ratio, i.e., a career, and a noise) is controlled as a result, and it can have the outstanding characteristic.

[0008]Although the melting point of Sn is about 232 **, the melting point of Sn-Bi alloy is about 139 **. Therefore, at the time of record by incidence of a laser beam, etc., the layer of Sn-Bi alloy is fused, since reactant high Sn serves as the liquid phase easily, it reacts to other layers close to Sn-Bi alloy layer easily, and it can obtain a high modulation factor. A modulation factor is the percentage to the reflectance before record of the value which subtracted the reflectance (B) after record from the reflectance (A) before record here. That is, it is the value which multiplied the value of (A-B)/A by 100%.

[0009]The field P where Sn-Bi with many Sn or the Sn component in this layer is detailed since Sn-Bi alloy is metal of eutectic crystal nature and the melting point is as low as about 139 ** when Sn-Bi alloy is formed as a recording layer. It comprises at least two or more phases with the detailed field Q of Bi or Sn-Bi with many Bi components. In this case, the field P has high reactivity, and since reactivity is low, the field Q can inhibit the reaction at the time of membrane formation with Sn-Bi alloy and other layers which approached by existence of the

field Q, when a recording layer is constituted from other layers laminated by approaching the layer and Sn-Bi of Sn-Bi alloy.
[0010]The optical recording medium (international application number PCT/JP98/04675, international publication number WO99/20472 reference) and recording layer which a recording layer turns into from the layer of Sn-Bi alloy and the layer of quality of an oxide, such as WO_3, from the former this invention person Then, the layer and GeSx of Sn-Bi alloy. Although the optical recording medium which consists of a layer of (1< x<=2) has been developed, improvement in the endurance in the improvement in the further endurance, especially heat-and-high-humidity environment is called for.
[0011]Then, the purpose of this invention is excellent in endurance, and there is in providing the optical recording medium excellent in the recording characteristic.
[0012]
[Means for Solving the Problem]Then, in an optical recording medium which this invention person has a recording layer, changes the optical property of this recording layer by giving external energy wholeheartedly as a result of research, and records information, the 1st layer in which said recording layer contains Sn and Bi -- this -- approaching with the 1st layer and giving external energy -- this -- the 1st layer and the 2nd layer that reacts, [have and] An optical recording medium, wherein an oxidizing zone containing quality of an oxide which oxidizes easilier than said Sn and said Bi is laminated at one [said both sides of the 1st layer or] side was invented.
[0013]That is, since a recording layer has the 1st layer that is a layer of Sn-Bi alloy, and this 2nd layer that reacts, by giving external energy, the optical recording medium of this invention can change the optical property of this recording layer remarkably, and can improve a recording characteristic.
[0014]In this case, since an optical recording medium of this invention uses Sn-Bi alloy for a recording layer, shape of the 1st layer which contains Sn-Bi alloy as mentioned above becomes what was ready. Since fine texture of the 1st layer is still the state where it comprised microscopic particles like the above, the noise level of an optical medium can control degradation of the C/N characteristic as a result, while it had been controlled by it.
[0015]The melting point of Sn-Bi alloy is about 139 **, at the time of record by incidence of a laser beam, etc., a layer of Sn-Bi alloy is fused and reactant high Sn serves as the liquid phase easily. Therefore, it becomes easy to react to the 2nd layer close to Sn-Bi alloy layer, and the optical recording medium of this invention can obtain a high modulation factor.
[0016]Sn-Bi alloy is metal of eutectic crystal nature, and since the melting point is as low as about 139 **, the 1st layer comprises at least two or more phases with Sn, the detailed fields P and Bi of Sn-Bi with many Sn components, or the detailed field Q of Sn-Bi with many Bi components. In this case, the field P has high reactivity, and since reactivity is low, the field Q

can inhibit a reaction at the time of non recording with the 2nd layer to which an optical recording medium of this invention approached Sn-Bi alloy and the 1st layer by existence of the field Q.

[0017]An optical recording medium of this invention has attained improvement in endurance, such as oxidation resistance, by laminating an oxidizing zone which contains in Sn-Bi alloy excellent in a recording characteristic quality of an oxide which oxidizes easilier than Sn and Bi to one [both sides of the 1st layer, or] side.

[0018]That is, by laminating an oxidizing zone containing quality of an oxide which oxidizes easilier than Sn and Bi to the 1st layer, quality of an oxide contained in an oxidizing zone can oxidize ahead of Sn and Bi, and corrosion by oxidation of Sn-Bi alloy, etc. can be controlled. A tunic of an oxide generated by oxidation of quality of an oxide is formed in an oxidizing zone, and also corrosion by oxidation of Sn-Bi alloy, etc. can be delayed. as a result, degradation of a recording layer at the time of non recording with the passage of time can be prevented, and the endurance of an optical recording medium can be boiled markedly and it can improve. It is preferred to use a substance which makes germanium and/or Ga a component at least as quality of an oxide. It is because germanium and/or Ga have [that it is easy to oxidize] the large effect over the oxidation resistance of a recording layer.

[0019]As for quality of an oxide, being added by the 1st layer is preferred. If quality of an oxide is added by the 1st layer, quality of an oxide will oxidize previously more nearly selectively than Sn-Bi alloy contained in the 1st layer, and corrosion by oxidation of Sn-Bi alloy, etc. will be delayed. A tunic of an oxide generated by oxidation of quality of an oxide is formed in the surface of Sn-Bi alloy, and also corrosion by oxidation of an optical recording medium, etc. can be delayed.

[0020]As for the 2nd layer of a recording layer, in an optical recording medium of this invention, it is preferred that it is a layer containing a substance which makes a component S, Se, a substance that makes one or more sorts of Te a component, or oxygen.

[0021]Namely, when the 2nd layer contains S, Se, and a substance that makes one or more sorts of Te a component, Since the 1st layer fuses and reactant high Sn serves as the liquid phase at the time of record by incidence of a laser beam, etc., Sn contained in the 1st layer, S contained in the 2nd layer, Se, and a substance which makes more than a kind a component at least among Te react, It is possible that a sulfide (SnS, SnS_2), a selenide (SnSe, $SnSe_2$), a telluride (SnTe), etc. are formed, a high modulation factor can be obtained, and it can have the outstanding recording characteristic.

[0022]When the 2nd layer contains a substance which makes oxygen a component, At the time of record by incidence of a laser beam, etc., the 1st layer fuses and an oxidation-reduction reaction produces it between substances which make a component Sn contained in the 1st layer and/or Bi, and oxygen contained in the 2nd layer, All or a part of Sn and/or Bi(s)

can be considered to change to an oxide, a high modulation factor can be obtained, and it can have the outstanding recording characteristic.
[0023]
[Embodiment of the Invention]The optical recording medium of this invention is an optical recording medium which changes the optical property of a recording layer physically and/or chemically, and records information by irradiating for example, with the laser beam for record, etc. as external energy. In this optical recording medium, it is usable to the optical disc, for example, CD-R, in which music, data, etc. are recorded, for example, DVD-R, etc.
[0024](A 1st embodiment) The optical recording medium of this embodiment, It is an optical recording medium which has a recording layer, changes the optical property of this recording layer by giving external energy, and records information, S which reacts to this 1st layer by this recording layer's approaching with the 1st layer containing Sn and Bi and this 1st layer, and giving external energy, The oxidizing zone containing the quality of an oxide which has the 2nd layer containing the substance which makes a component more than a kind of Se and Te, and oxidizes easilier than Sn and Bi is the optical recording medium laminated at one [the both sides of the 1st layer, or] side. This embodiment is described below.
[0025]The optical recording medium of this embodiment can laminate and constitute a substrate, a recording layer, an oxidizing zone, and a protective layer.
[0026]A substrate bears a recording layer and a protective layer, and consists of a transparent material which can penetrate the irradiation light for record, reproduction, etc. So, the material of a substrate can be chosen according to irradiation light. Usually, a laser beam is used as the irradiation light. In that case, what is necessary is just to choose the material which can penetrate a laser beam. As the material, transparent resin, such as polycarbonate, polyethylene terephthalate (PET), and an acrylic, can be used. These resin is excellent in the lightweight point. Or transparent glass may be used. Glass is excellent in the point that a mechanical strength is high.
[0027]What is necessary is just to choose according to the use of an optical recording medium about the shape of a substrate. About especially thickness, it is preferred that the mechanical strength which an optical recording medium needs is obtained.
[0028]The track (guide rail) to which it shows a laser beam can be formed in the field where the recording layer of a substrate is laminated. What is necessary is for what is necessary to be just to form the shape of a track appropriately according to the shape of an optical storage medium, a use, etc., and just to form it in concentric circle shape or spiral shape in a disc-like optical recording medium.
[0029]A recording layer is a layer on which the optical property is changed and information is recorded. The optical property of this recording layer is changed and information is recorded. In the optical recording medium of this embodiment, a recording layer approaches with the 1st

layer containing Sn and Bi and this 1st layer, it has the 2nd layer containing S, Se, and the substance that makes a component at least one or more sorts in Te, and these 1st layer and the 2nd layer react mutually by grant of external energy.

[0030]Sn and Bi are used for the 1st layer. Since the melting point of Sn-Bi alloy is about 139 **, the 1st layer containing Sn-Bi alloy fuses at the time of record by incidence of a laser beam, etc. and reactant high Sn becomes the liquid phase easily, it can react to the 2nd layer that approaches easily. Sn-Bi alloy can lower the noise level of an optical recording medium, as mentioned above, and it can control degradation of the C/N characteristic. The substance which makes a component chalcogen elements, such as what is called S, Se, and Te, at the 2nd layer, For example, GeSx ($1< x<=2$), Y_5S_7, $La_2O_2S_2$, $Ce_2O_2S_2$, GeSex ($1< x<=2$), SeS, ZnSe, ZnTe, PbTe, TeI_2, etc. can be used.

[0031]In this embodiment, Sn-Bi alloy contained in the 1st layer by the exposure of the laser beam at the time of record, etc. is fused, and serves as melt mostly, and Sn with high reactivity can carry out a direct reaction to the substance which makes S, Se, Te, etc. a component. Since Sn serves as the liquid phase, a reaction with the substance which makes a component at least one or more sorts of Sn, S, Se, and Te turns into a reaction of the reactant high liquid phase and solid phase rather than the reaction of solid phase, It will become easy to carry out a chemical reaction to S, Se, Te, etc., and a sulfide (SnS, SnS_2), a selenide (SnSe, $SnSe_2$), a telluride (SnTe), etc. will be generated. As a result, the optical properties (reflectance etc.) of a recording layer can change, and information can be recorded. Thus, when a recording layer has the 1st layer that reacts mutually, and the 2nd layer, the optical property of a recording layer can be changed remarkably, a high modulation factor can be obtained, and a recording characteristic can be improved remarkably.

[0032]Sn-Bi alloy is existence of the detailed field Q of reactant low Bi or Sn-Bi with many Bi components, as mentioned above. The reaction at the time of non recording with the 2nd layer containing the 1st layer, S, Se, and the substance that makes a component at least one or more sorts in Te can be inhibited.

[0033]The 3rd layer that contains ZnS, Si, SiO_2, SiNx ($1< x<1.5$), C, hydrocarbon, etc. between these 1st layer and the 2nd layer can be laminated. By making the 3rd layer intervene between the 1st layer and the 3rd layer, the 1st layer [at the time of non recording] and 2nd-layer reaction can be inhibited further, and degradation of a recording characteristic can be controlled more efficiently.

[0034]These recording layers are not limited and can make especially thickness suitable thickness. What is necessary is for what is necessary to be for the thickness of the 1st layer just to be 10-100 nm in general, and for the thickness of the 2nd layer just to be 20-250 nm in general, since the recording layer is laminated in this embodiment. Although what is necessary

is just to choose the thickness of the 3rd layer appropriately, in order for the 3rd layer to fully pull out the characteristic as a layer which inhibits a reaction, 0.5-5 nm is preferred.

[0035]Formation of a recording layer can be performed using publicly known methods, such as a sputtering technique and a vacuum deposition method.

[0036]An oxidizing zone is a layer containing the quality of an oxide which oxidizes easilier than Sn and Bi, and is laminated at one [the both sides of the 1st layer, or] side. The oxidation resistance of the 1st layer can be improved by laminating an oxidizing zone to one [the both sides of the 1st layer, or] side. That is, the quality of an oxide contained in an oxidizing zone can oxidize ahead of Sn and Bi, and the corrosion by oxidation of Sn-Bi alloy, etc. can be controlled. The tunic of the oxide generated when the quality of an oxide oxidized is formed in an oxidizing zone, and also the corrosion by oxidation of Sn-Bi alloy, etc. can be delayed. as a result, degradation of the recording layer at the time of non recording with the passage of time can be prevented, and the endurance of an optical recording medium can be boiled markedly and it can improve.

[0037]As quality of an oxide used for an oxidizing zone, Ga, germanium, an alkaline metal, alkaline-earth metals, a rare earth metal, Ti, Cr, nickel, etc. can be used. In this case, an alloy compound can also be alone used like germanium, Ga, and Cr like Ti_2 Ga, In-Mg, and Ta-La. In this case, it is preferred to use the substance which makes germanium and/or Ga a component at least as quality of an oxide. It is because germanium and Ga oxidize easily and their effect over the oxidation resistance of a recording layer is large.

[0038]Generally the thickness of an oxidizing zone can be 0.5-30 nm, and its 1-10 nm is preferred. Although the endurance of an optical recording medium improves by laminating an oxidizing zone, the improvement in endurance is remarkable in especially thickness being 1 nm or more. However, since it will become easy to produce characteristic degradation, such as a recording characteristic, for example, C/N, reflectance, and record power, if thickness is set to not less than 10 nm, forming in the thickness beyond this is not preferred.

[0039]Formation of an oxidizing zone can be performed by publicly known methods, such as a sputtering technique, a vacuum deposition method, and a spraying process.

[0040]It is preferred to add the quality of an oxide which oxidizes easilier than Sn and Bi to the 1st layer containing Sn and Bi. As mentioned above, germanium, Ga, a rare earth metal, etc. can be used as this quality of an oxide. It is preferred to use germanium and/or Ga similarly. By adding the quality of an oxide which oxidizes easilier to Sn-Bi alloy than Sn, the Sn-Bi alloy itself can be reformed and the oxidation resistance of Sn-Bi alloy can be improved. That is, by adding the quality of an oxide which oxidizes easilier to Sn-Bi alloy than Sn, this quality of an oxide can oxidize ahead of Sn and Bi, and the corrosion by oxidation of Sn-Bi alloy, etc. can be controlled. The tunic of the oxide which this quality of an oxide oxidized and generated is formed in the surface of Sn-Bi alloy, and also the corrosion by oxidation etc. can be delayed.

as a result, the endurance of an optical recording medium can be boiled markedly, and it can improve.

[0041]It is necessary to make into a suitable quantity the rate of the quality of an oxide which oxidizes easilier than Sn and Bi. It becomes impossible that is, to demonstrate the outstanding endurance mentioned above when there was too little quantity of the quality of an oxide. When there is too much quantity of the quality of an oxide on the contrary, it is in having big influence on the characteristic of Sn-Bi alloy which is a hardener, especially the melting point, the crystalline particle diameter at the time of membrane formation, etc., and the recording characteristic of an optical recording medium is made to deteriorate by addition of the quality of an oxide. When adding Ga to Sn-Bi alloy and there are many additions, the melting point is made to fall remarkably, the fall of the C/N characteristic is caused, and it becomes impossible for example, to use it as the real above-mentioned recording media. When adding germanium and there are many additions on the other hand, the melting point is made to rise remarkably, the rise of record power is caused, or decline in reflectance, etc. are caused, and it becomes impossible to use it as a real Uemitsu recording medium too.

[0042]Therefore, when the presentation of Bi uses as a hardener Sn-Bi alloy which is 30-70atom%, the addition of Ga makes all the ingredients 100 atom %, its 0.05-30 atom % is preferred, the addition of germanium makes all the ingredients 100 atom %, and 0.01-2 atom % is preferred [an addition].

[0043]A protective layer is a layer which protects a recording layer. For example, a protective layer can be formed using ultraviolet curing resin with a spin coat method.

[0044](A 2nd embodiment) The optical recording medium of this embodiment, It is an optical recording medium which has a recording layer, changes the optical property of this recording layer by giving external energy, and records information, It has the 2nd layer containing the substance which makes a component the oxygen which reacts to this 1st layer by this recording layer's approaching with the 1st layer containing Sn and Bi and this 1st layer, and giving external energy, The oxidizing zone containing the quality of an oxide which oxidizes easilier than Sn and Bi is the optical recording medium laminated at one [the both sides of the 1st layer, or] side. Namely, at this embodiment, the 2nd layer of the recording layer differs from the case of a 1st embodiment in that it is a layer containing the substance which makes oxygen a component. It explains focusing on a below different portion from a 1st embodiment.

[0045]The optical recording medium of this embodiment can laminate and constitute a substrate, a recording layer, an oxidizing zone, and a protective layer.

[0046]The same substrate as the substrate of a 1st embodiment can be used for a substrate. Therefore, explanation of a 1st embodiment carries out appropriate.

[0047]The recording layer of this embodiment is the same as that of a 1st embodiment by giving external energy at the point of having the 1st layer that reacts mutually, this 1st layer,

and the 2nd approaching layer.
[0048]The 1st layer is a layer containing Sn and Bi, and is the same as that of the 1st layer of a 1st embodiment. Therefore, explanation by a 1st embodiment carries out appropriate.
[0049]The 2nd layer of this embodiment is a layer containing the substance which makes oxygen a component. Six fellows, such as Cr [in / in the 2nd layer / the periodic table of an element], Mo, and W, Fe, The substance which makes a component oxygen, such as an oxide which contains at least one element among 11 fellows, such as nine fellows, such as eight fellows, such as Ru, Co, Rh, and Ir, Cu, Ag, and Au, and Ti and V, Mn, nickel, Re, Cd, As, germanium, Pb, Se, Te, Ce, Pr, and Tb, can be used. For example, WO_3, MoO_3, Rh_2O_3, Oxides, such as TiO_2 and As_2O_3, GeO_2, SeO_2, and CeO_2, GeON, $Ce(OH)_4$, $AgIO_3$, etc. can be used.
[0050]When the 2nd layer contains the substance which makes oxygen a component, At the time of record by incidence of a laser beam, etc., the 1st layer fuses and an oxidation-reduction reaction produces it between the substances which make a component Sn contained in the 1st layer and/or Bi, and the oxygen contained in the 2nd layer, All or a part of Sn and/or Bi(s) are considered to change to oxides, such as SnO and Bi_2O_3. Thus, when a recording layer has the 1st layer that reacts mutually, and the 2nd layer, the optical property of a recording layer can be changed remarkably, a high modulation factor can be obtained, and a recording characteristic can be improved remarkably.
[0051]Since the substance in which the substance after a reaction contains oxygen, such as an oxide, as a component exists, a reaction front stirrup is strongly excellent in a resistance to environment by heat, humidity, etc., and tends to inhibit an unnecessary reaction at the time of non recording.
[0052]The energy (henceforth oxygen bond energy) generated when Sn combines with the amount of 1 mol of oxygen molecules is 610kJ in general. Therefore, it is preferred to use the substance which makes a component oxygen, such as an oxide which is 550 or less kJ about energy (henceforth oxygen dissociation energy) required when dissociating 1 mol of oxygen molecules, as a substance which makes a component oxygen, such as an oxide contained in the 2nd layer. Since the oxygen bond energy of the 1st layer is larger than the oxygen dissociation energy of the 2nd layer, the 1st layer and 2nd-layer reaction can turn into an exoergic reaction, a reaction cannot go to an opposite direction, and the holding property of record data can be secured. If oxygen dissociation energy exceeds 550kJ, oxygen will dissociate and reactivity will fall in ****. For example, As_2O_3, SeO_2, CeO_2, and Rh_2O_3, MoO_3, TiO_2, WO_3, etc. are preferred.
[0053]As mentioned above, oxides, such as all [of Sn and/or Bi(s)]/or the part included in the

1st layer by the exposure of a laser beam, etc., and WO_3 contained in the 2nd layer, etc. produce an oxidation-reduction reaction, and the oxide of Sn and/or Bi generates. Therefore, the optical properties (reflectance etc.) of a recording layer can change and information can be recorded.

[0054]The 3rd layer that contains C (carbon), hydrocarbon, Si, SiNx (1<x1.5), Ti, W, Zr, etc. between these 1st layer and the 2nd layer can be laminated. By making the 3rd layer intervene between the 1st layer and the 3rd layer, the 1st layer [at the time of non recording] and 2nd-layer reaction can be inhibited, and degradation of a recording characteristic can be controlled more efficiently.

[0055]These recording layers are not limited and can make especially thickness suitable thickness. What is necessary is for what is necessary to be for the thickness of the 1st layer just to be 10-100 nm in general; and for the thickness of the 2nd layer just to be 10-250 nm in general. Although what is necessary is just to choose the thickness of the 3rd layer appropriately, in order for the 3rd layer to fully pull out the characteristic as a layer which inhibits a reaction, 0.5-10 nm is preferred.

[0056]Formation of a recording layer can be performed like a 1st embodiment using publicly known methods, such as a sputtering technique and a vacuum deposition method.

[0057]The oxidizing zone is the same as that of the case of a 1st embodiment. Therefore, explanation by a 1st embodiment carries out appropriate. That is, it is a layer containing the quality of an oxide which oxidizes easilier than Sn and Bi, and laminates at one [the both sides of the 1st layer, or] side. It is preferred to use the substance which can use germanium, Ga, an alkaline metal, alkaline-earth metals, a rare earth metal, Ti, Cr, nickel, etc., and makes germanium and/or Ga a component at least like the case of a 1st embodiment also with the quality of an oxide used for an oxidizing zone. Generally the thickness of an oxidizing zone can be 0.5-30 nm, and one with preferred 1-10 nm of it is the same as that of the case of a 1st embodiment. Formation of an oxidizing zone can be performed by publicly known methods, such as a sputtering technique, a vacuum deposition method, and a spraying process.

[0058]It is preferred to add the quality of an oxide which oxidizes easilier than Sn and Bi to the 1st layer containing Sn and Bi. It is the same as that of the case of a 1st embodiment. Therefore, explanation by a 1st embodiment carries out appropriate. That is, it is preferred to use germanium and/or Ga which can use germanium, Ga, a rare earth metal, etc. as this quality of an oxide. When it is necessary to make into a suitable quantity the rate of the quality of an oxide which oxidizes easilier than Sn and Bi and the presentation of Bi uses as a hardener Sn-Bi alloy which is 30-70atom%, the addition of Ga makes all the ingredients 100 atom %, 0.05-30 atom % is preferred, the addition of germanium makes all the ingredients 100 atom %, and its 0.01-2 atom % is preferred.

[0059]A protective layer is a layer which protects a recording layer. It is the same as that of the

case of a 1st embodiment, for example, a protective layer can be formed using ultraviolet curing resin with a spin coat method.
[0060](Other embodiments) The embodiment of the optical recording medium of this invention, In the optical recording medium which has a recording layer, changes the optical property of this recording layer by giving external energy, and records information, the 1st layer in which a recording layer contains Sn and Bi -- this -- the 1st layer and the 2nd layer that reacts by approaching with the 1st layer and giving external energy, [have and] If the oxidizing zone containing the quality of an oxide which oxidizes easilier than Sn and Bi is the optical recording medium laminated at one [said both sides of the 1st layer, or] side, it will not be restricted to 1st and 2nd embodiments of the above.
[0061]For example, as long as the 2nd layer of a recording layer reacts to the 1st layer, it may laminate layers other than the composition described by 1st and 2nd embodiments.
[0062]The 1st layer containing Sn and Bi can also be made to add Ag, Au, In, etc.
[0063]The external energy in particular to which the optical property of a recording layer is changed is not limited to a laser beam. They may be the optical whole, electromagnetic waves, etc.
[0064]
[Example]Based on an example, the optical recording medium of this invention is explained below. A comparative example is also indicated for comparison with an example.
[0065][Example 1] In the optical recording medium which the optical recording medium of this example 1 has [optical recording medium] a recording layer, changes the optical property of this recording layer by giving external energy, and records information, It has the 1st layer and the 2nd layer that reacts by this recording layer's approaching the 1st layer containing Sn and Bi and this 1st layer, and giving external energy, This 2nd layer is an optical recording medium with which the oxidizing zone which consists of germanium as quality of an oxide which oxidizes easilier than Sn and Bi including WO_3 as a substance which makes oxygen a component is laminated by the both sides of the 1st layer. In this example 1, the laser beam was used as external energy. The partial section composition of the optical recording medium concerning this example 1 is shown in drawing 1.
[0066]The optical recording medium 100 of this example 1 is carrying out the disc-like gestalt as a whole. it is shown in drawing 1 -- as -- the 1st of the substrate 10, the oxidizing zone 50, and a recording layer -- layer 20, the oxidizing zone 50, and a recording layer -- laminating formation of the 2nd layer of 30 and the protective layer (resin layer) 60 is carried out. The substrate 10 is a 1.2-mm-thick transparent product made from polycarbonate, and is formed disc-like. The laser beam for record of light information and reproduction enters like the arrow A from the one direction 10a of a substrate. The track (guide rail) 10c of the spiral shape for [which is a laser beam incidence side of the substrate 10] the field 10a being a smooth side

and on the other hand, leading a laser beam to the another side side 10b is formed.
[0067]the germanium film 50a is laminated as the oxidizing zone 50 on the another side side 10b of the substrate 10 -- an it top -- a recording layer -- the 1st layer of Sn-43-atom % Bi film 20a is laminated as 20. The germanium film 50b is laminated as the oxidizing zone 50 on this Sn-43-atom % Bi film 20a again. this germanium film 50b top -- a recording layer -- the 2nd layer of the WO_3 film 30a is laminated as 30. That is, it is the composition that the germanium films 50a and 50b which are the oxidizing zones 50 are laminated by the substrate 10 side of Sn-43-atom % Bi film 20a of a recording layer which is 20 the 1st layer, and the substrate 10 and an opposite hand. In order to cover and protect a recording layer on the WO_3 film 30a of a recording layer which is 30 the 2nd layer, the protective layer (resin layer) 60 which consists of ultraviolet curing resin is formed.
[0068]The optical recording medium of Example 1 was produced as follows.
[0069]The disc-like substrate 10 made from polycarbonate which is 1.2 mm in thickness by which the smooth side was formed in the field 10a, and the track 10c was first formed in the another side side 10b on the other hand was prepared. This track 10c was formed, and also 5 nm of germanium films 50a were formed by RF sputtering technique on the direction 10b using germanium target by the film formation condition of sputtering gas kind:Ar, sputtering gas pressure:$4x10^{-1}$Pa, and supplied power:250W.
[0070]Next, 70 nm of Sn-43-atom % Bi films 20a were formed by DC sputtering technique using the Sn-43-atom %Bi target in the film formation condition of sputtering gas kind:Ar, sputtering gas pressure:$4x10^{-1}$Pa, and supplied power:500W on this germanium film 50a.
[0071]1 nm of germanium films 50b were further formed by RF sputtering technique using germanium target in the film formation condition of sputtering gas kind:Ar, sputtering gas pressure:$4x10^{-1}$Pa, and supplied power:250W on this Sn-43-atom % Bi film 20a.
[0072]20 nm of WO_3 films 30a were formed by DC sputtering technique using WO_3 target in sputtering gas kind:O_2, sputtering gas pressure:$5x10^{-1}$Pa, and a supplied power:4kW film formation condition on this germanium film 50b.
[0073]Finally ultraviolet curing resin was applied with the spin coat method, this ultraviolet curing resin was stiffened using the high-pressure mercury lamp, the protective layer (resin layer) 60 was formed, and the optical recording medium 100 of this example 1 was produced.
[0074]The recording characteristic of the optical recording medium 100 produced by this example 1 was checked.
[0075]On the other hand, NA (numerical aperture) recorded the laser beam whose wavelength is 780 nm from the field 10a side on the optical recording medium 100 of Example 1 by letting the object lens of 0.5 pass and condensing on an Sn-43-atom % Bi film 20a side. Carrying out

linear velocity in 5.6 m/sec, recording frequency made 800 kHz and a record laser waveform the square wave of 50% of duty ratio. As for the characteristic of the optical recording medium 100 at this time, 60% and the recording laser power were 55 dB in the non-Records Department reflectance of 15 mW and C/N, and were 75% in the modulation factor.
[0076]The optical recording medium 100 recorded [this] was held under the environment of the temperature of 60 **, and 90% of relative humidity as an environmental test-proof for 120 hours. When C/N, the non-Records Department reflectance, and a modulation factor were measured after this, any characteristic could check that change was not accepted by error-of-measurement within the limits, and the holding property of good record data was shown.
[0077][Example 2] In the optical recording medium which the optical recording medium of this example 2 has [optical recording medium] a recording layer, changes the optical property of this recording layer by giving external energy, and records information, It has the 1st layer and the 2nd layer that reacts by this recording layer's approaching the 1st layer containing Sn and Bi and this 1st layer, and giving external energy, germanium is added by this 1st layer as quality of an oxide which oxidizes easilier than Sn and Bi, This 2nd layer is an optical recording medium with which the oxidizing zone which consists of germanium as quality of an oxide which oxidizes easilier than Sn including WO_3 as a substance which makes oxygen a component is laminated by the both sides of the 1st layer. That is, the difference from Example 1 is the point that germanium was added by the 1st layer as quality of an oxide. The partial section composition of the optical recording medium applied to this example 2 using drawing 1 is shown.
[0078]Production of the optical recording medium 100 of Example 2 was produced by the same method as the optical recording medium of Example 1 except [of the recording layer] having used the 1st layer of the Sn-42.5-atom %Bi-one-atom %germanium film 20b as 20. Therefore, it limits for indicating the film formation condition of the Sn-42.5-atom %Bi-one-atom %germanium film 20b here.
[0079]70 nm of Sn-42.5-atom %Bi-one-atom %germanium films 20b formed membranes by DC sputtering technique using the Sn-42.5-atom %Bi-one-atom %germanium target in the film formation condition of sputtering gas kind:Ar, sputtering gas pressure:$4x10^{-1}$Pa, and supplied power:500W.
[0080]The recording characteristic of the optical recording medium 100 produced by this example 2 was checked.
[0081]On the other hand, NA (numerical aperture) recorded the laser beam whose wavelength is 780 nm from the field 10a side on the optical recording medium 100 of Example 2 by letting the object lens of 0.5 pass and condensing on an Sn-42.5-atom %Bi-one-atom %germanium film 20b side. Carrying out linear velocity in 5.6 m/sec, recording frequency made 800 kHz and a record laser waveform the square wave of 50% of duty ratio. As for the characteristic of the

optical recording medium 100 at this time, 60% and the recording laser power were 52 dB in the non-Records Department reflectance of 15 mW and C/N, and were 71% in the modulation factor.

[0082]The optical recording medium 100 recorded [this] was held under the environment of the temperature of 60 **, and 90% of relative humidity as an environmental test-proof for 120 hours. When C/N, the non-Records Department reflectance, and a modulation factor were measured after this, any characteristic could check that change was not accepted by error-of-measurement within the limits, and the holding property of good record data was shown.

[0083]About the optical recording medium 100 recorded [this], the environmental test-proof severer than the above-mentioned environmental test-proof was done. Namely, it held under the environment of the temperature of 70 **, and 95% of relative humidity for 48 hours. When C/N, the non-Records Department reflectance, and a modulation factor were measured after this, any characteristic could check that change was not accepted by error-of-measurement within the limits, and the holding property of good record data was shown.

[0084][Example 3]

(Example 3) In the optical recording medium which the optical recording medium of this example 3 has [optical recording medium] a recording layer, changes the optical property of a recording layer by giving external energy, and records information, the 1st layer in which a recording layer contains Sn and Bi -- this -- approaching with the 1st layer and giving external energy -- this -- it has the 1st layer and the 2nd layer that reacts, and germanium is added by this 1st layer as quality of an oxide which oxidizes easilier than Sn and Bi.

The 2nd layer contains GeS_2 as a substance which makes a component one or more sorts in S, Se, and Te, The 3rd layer containing ZnS-SiO_2 is laminated between this 1st layer and this 2nd layer, and the oxidizing zone which consists of Ti_2 Ga as an oxidizing zone containing the quality of an oxide which oxidizes easilier than Sn and Bi is the optical recording medium laminated at one 1st layer side.

The laser beam was used for the optical recording medium of this example 3 as external energy. The partial section composition of the optical recording medium concerning this example 3 is shown in drawing 2. The same numerals as drawing 1 were used about the element of the same kind about the numerals used for drawing 2.

[0085]The optical recording medium 200 of this example 3 is carrying out the disc-like gestalt as a whole. it is shown in drawing 2 -- as -- the 2nd of the substrate 10 and a recording layer -- the 3rd of layer 30 and a recording layer -- layer 40 and a recording layer -- laminating formation of the 1st layer of 20, the oxidizing zone 50, and the protective layer (resin layer) 60 is carried out. The substrate 10 is a 1.2-mm-thick transparent product made from polycarbonate, and is formed disc-like. The laser beam for record of light information and

reproduction enters like the arrow A from the one direction 10a of a substrate. The track (guide rail) 10c of the spiral shape for [which is a laser beam incidence side of the substrate 10] the field 10a being a smooth side and on the other hand, leading a laser beam to the another side side 10b is formed.

[0086]the another side side 10b top of the substrate 10 -- a recording layer -- the 2nd layer of the GeS_2 film 30b is laminated as 30 -- an it top -- a recording layer -- the 3rd layer of the Zn-20 mol %SiO_2 film 40a is laminated as 40. this Zn-20 mol %SiO_2 film 40a top -- further -- a recording layer -- the 1st layer of the Sn-42.5-atom %Bi-one-atom %germanium film 20c is laminated as 20. The Ti_2Ga film 50c is laminated as the oxidizing zone 50 on this Sn-42.5-atom %Bi-one-atom %germanium film 20c. That is, it is the composition that the Ti_2Ga film 50c which is the oxidizing zone 50 is laminated by the substrate 10 and opposite hand of the Sn-42.5-atom %Bi-one-atom %germanium film 20c which is 20 the 1st layer of a recording layer.

[0087]In order to cover and protect a recording layer on the Sn-42.5-atom %Bi-one-atom % germanium film 20c of a recording layer which is 20 the 1st layer, the protective layer (resin layer) 60 which consists of ultraviolet curing resin is formed.

[0088]The optical recording medium 200 of Example 3 was produced as follows.

[0089]The disc-like substrate 10 made from polycarbonate which is 1.2 mm in thickness by which the smooth side was formed in the field 10a, and the track 10c was first formed in the another side side 10b on the other hand was prepared. This track 10c was formed, and also 167 nm of GeS_2 films 30b were formed by RF sputtering technique on the direction 10b using germanium target by the film formation condition of sputtering gas kind:Ar, sputtering gas pressure:$4x10^{-1}$Pa, and supplied power:500W.

[0090]Next, on this GeS_2 film 30b by RF sputtering technique. the ZnS-20 mol %SiO_2 film 40a -- sputtering gas kind: -- 2 nm formed membranes using the ZnS-20 mol %SiO_2 target in the film formation condition of Ar, sputtering gas pressure:$4x10^{-1}$Pa, and supplied power:250W.

[0091]On the ZnS-20 mol %SiO_2 film 40a, by DC sputtering technique. the Sn-42.5-atom %Bi-one-atom %germanium film 20c -- sputtering gas kind: -- 60 nm formed membranes using the Sn-42.5-atom %Bi-one-atom %germanium target in the film formation condition of Ar, sputtering gas pressure:$4x10^{-1}$Pa, and supplied power:500W.

[0092]On this Sn-42.5-atom %Bi-one-atom %germanium film 20c, by DC sputtering technique. 2 nm of Ti_2Ga films 50c were formed using the Ti_2Ga target in the film formation condition of sputtering gas kind:Ar, sputtering gas pressure:$4x10^{-1}$Pa, and supplied power:500W.

[0093]Finally ultraviolet curing resin was applied with the spin coat method, this ultraviolet

curing resin was stiffened using the high-pressure mercury lamp, the protective layer (resin layer) 60 was formed, and the optical recording medium 200 of this example 3 was produced.
[0094]The recording characteristic of the optical recording medium 200 produced by this example 3 was checked.
[0095]On the other hand, NA (numerical aperture) recorded the laser beam whose wavelength is 780 nm from the field 10a side on the optical recording medium 200 of Example 3 by letting the object lens of 0.5 pass and condensing on an Sn-42.5-atom %Bi-one-atom %germanium film 20c side. Carrying out linear velocity in 5.6 m/sec, recording frequency made 800 kHz and a record laser waveform the square wave of 50% of duty ratio. As for the characteristic of the optical recording medium at this time, 62% and the recording laser power were 55 dB in the non-Records Department reflectance of 13 mW and C/N, and were 82% in the modulation factor.
[0096]The optical recording medium 200 recorded [this] was held under the environment of the temperature of 60 **, and 90% of relative humidity as an environmental test-proof for 120 hours. When C/N, the non-Records Department reflectance, and a modulation factor were measured after this, any characteristic could check that change was not accepted by error-of-measurement within the limits, and the holding property of good record data was shown.
[0097]An oxidizing zone may be further added between the substrate 10 and the GeS_2 film 30b at this time.
[0098](Comparative example 1) The optical recording medium of the comparative example 1 forms 60 nm of Sn-43-atom % Bi films instead of the Sn-42.5-atom %Bi-one-atom % germanium film which is the 1st layer of the recording layer of the optical recording medium of Example 3, and is an optical recording medium except the Ti_2Ga film which is an oxidizing zone. Next fundamental composition is the same as that of Example 3. The partial section composition of the optical recording medium concerning this comparative example 1 is shown in drawing 3. The same numerals as drawing 2 were used about the element of the same kind about the numerals used for drawing 3. namely, the optical recording medium 300 of the comparative example 1 -- the 2nd of the substrate 10 and a recording layer -- the 3rd of layer 30 (GeS_2 film 30b) and a recording layer -- layer 40 (Zn-20 mol $\%SiO_2$ film 40a) and a recording layer -- a protective layer with 20 (Sn-43-atom % Bi film 20d) the 1st layer. (Resin layer) Laminating formation of 60 is carried out.
[0099]Production of the optical recording medium 300 of the comparative example 1 was produced by the same method as the optical recording medium 200 of Example 3 except not having laminated the Ti_2Ga film 50c which are the thing of a recording layer for which the 1st layer of Sn-43-atom % Bi film 20d was used as 20, and the oxidizing zone 50.
[0100]Therefore, it limits for indicating the film formation condition of Sn-43-atom % Bi film 20d

here. 60 nm of Sn-43-atom % Bi films 20d formed membranes by DC sputtering technique using the Sn-43-atom %Bi target in the film formation condition of sputtering gas kind:Ar, sputtering gas pressure:$4x10^{-1}$Pa, and supplied power:500W.

[0101]The recording characteristic of the optical recording medium 300 produced by the comparative example 1 was checked.

[0102]On the other hand, NA (numerical aperture) recorded the laser beam whose wavelength is 780 nm from the field 10a side on the optical recording medium 300 of the comparative example 1 by letting the object lens of 0.5 pass and condensing on an Sn-43-atom % Bi film 20d side. Carrying out linear velocity in 5.6 m/sec, recording frequency made 800 kHz and a record laser waveform the square wave of 50% of duty ratio. As for the characteristic of the optical recording medium 300 at this time, 63% and the recording laser power were 56 dB in the non-Records Department reflectance of 13 mW and C/N, and were 83% in the modulation factor.

[0103]In the optical recording medium 300 recorded [this], when the same environmental test-proof as Example 3 was carried out, the non-Records Department reflectance became 20% or less, and degradation of the clear recording characteristic was accepted.

[0104]

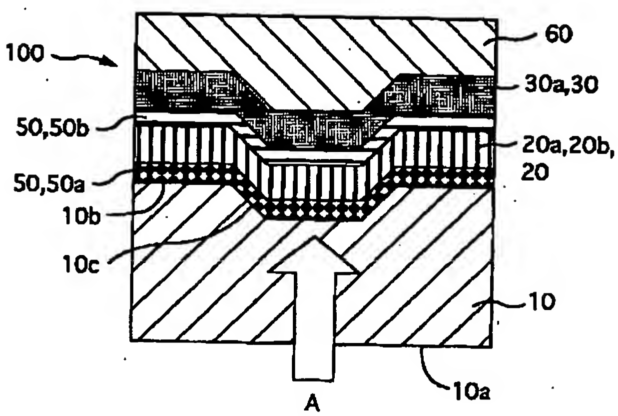
[Effect of the Invention]Since the recording layer has the 1st layer containing Sn and Bi, this 1st layer, and the 2nd layer that reacts, the optical recording medium of this invention is easy to change an optical property, and can demonstrate the effect excellent in recording characteristics, such as reflectance. Since the oxidizing zone which contains in the 1st layer of a recording layer the quality of an oxide which oxidizes easilier than Sn and Bi is laminated, the outstanding endurance can be improved. When the substance which makes Ga and/or germanium a component at least is used as quality of an oxide, improvement in endurance is remarkable. When [of the 1st layer] it adds, endurance improves the quality of an oxide further.

[0105]When the 2nd layer of a storage layer is a layer containing the substance which makes a component the substance which makes a component one or more sorts in S, Se, and Te, or oxygen, while the optical recording medium of this invention is excellent in endurance, it can demonstrate the effect which was excellent also in recording characteristics, such as reflectance, again.

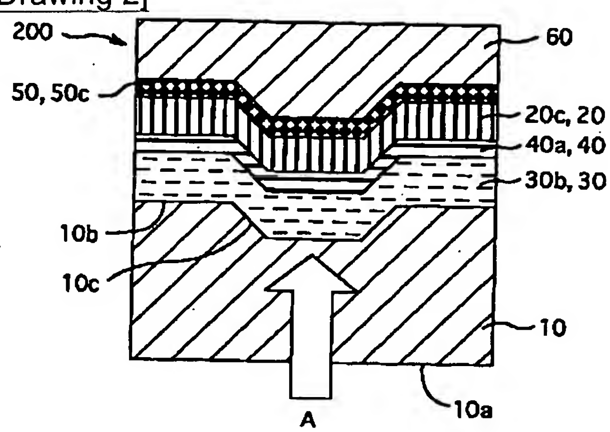
[Translation done.]

DRAWINGS

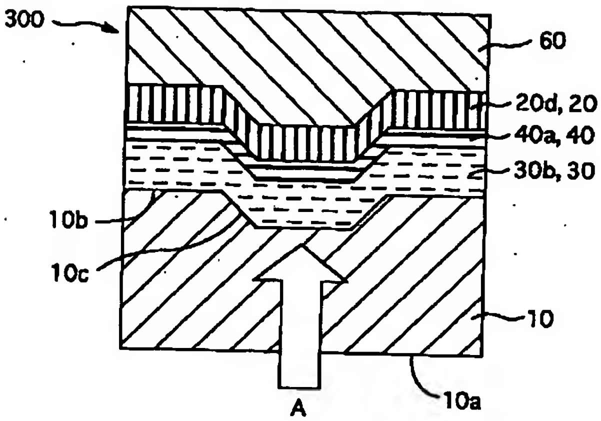
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]